BOND DELOCALIZABILITIES OF LINEAR CHAINS

MAKOTO ISIHARA

This paper analyzes bond delocalizabilities of even-membered linear chains noncomputationally. Bond delocalizabilities between different-color sites are essentially Ruedenberg bond orders, calculated easily for linear chains by inverting the adjacency matrix. As for bond delocalizabilities between identical-color sites, a reduction formula is prepared to express them in terms of superdelocalizabilities of linear chains and used together with an analytic expression of the superdelocalizabilities to provide a plain analytic expression to the bond delocalizabilities. Behaviors of bond delocalizabilities in linear chains are examined by using the analytic expression, the reduction formula, and asymptotic estimates of superdelocalizabilities in long linear chains. Basic features of the bond delocalizabilities are fully clarified in quite a simple way.

1. Introduction

In the previous paper (Isihara, 1997) on a noncomputational analysis of superdelocalizabilities of even-membered linear chains, the author derived an analytic expression of the superdelocalizabilities. This analytic expression was used to examine behaviors of superdelocalizabilities in long linear chains and led us to a few asymptotic expressions of the superdelocalizabilities (Isihara, 1997; Hosoya and Iwata, 1999). The present paper concerns bond delocalizabilities (Fukui, Imamura, Yonezawa and Nagata, 1961) of even-membered linear chains. Bond delocalizability cannot be regarded necessarily as a "direct" index of reactiviy and seems far from being prevalent. It will be not futile, however, to know basic features of this quantity in such typical systems as linear chains. In what follows, no confusion being expected, the word "even-membered" is omitted for brevity, "superdelocalizability" and "bond delocalizability" are abbreviated to SD and BD, respectively, and the parity with respect to alternant symmetry is referred to simply as color.

The next section is preliminary, giving a concise description of a few general properties of BDs. The subsequent section derives an analytic expression of BDs of linear chains. BDs between different-color sites are essentially Ruedenberg bond orders (Ruedenberg, 1954) and can be calculated easily for linear chains, say, by inverting the adjacency matrix. As for BDs between identical-color sites, a reduction formula relating them to SDs of linear chains is derivable from the hypervirial condition (Isihara, 1989, 1991a) upon BDs, so that the analytic expression of the SDs previously obtained suffices to provide an analytic expression to BDs between identical-color sites. The last section examines behaviors of BDs of linear chains by using the analytic expression, the reduction formula, and asymptotic estimates of SDs in long linear chains, clarifying basic features of BDs of linear chains.

2. Preliminaries

Consider a Hückel system specified solely by adjacency of sites and assume the adjacency matrix $\boldsymbol{A}$ of the system to be regular. Denote the j-th column eigenvector of $\boldsymbol{A}$ by $\boldsymbol{C}_j$ and its eigenvalue by λ_j. We can assume $\{\boldsymbol{C}_j\}$ to form a complete orthonormal set. Let us confine ourselves to the normal state in which each orbital j of positive λ_j is doubly occupied and others are unoccupied. Then, introducing the auxiliary index g taking the values 1, 0, and -1, respectively, for electrophilic, radical, and nucleophilic reactions, we can define the SD matrix $\boldsymbol{S}^{(g)}$ as

$$\boldsymbol{S}^{(g)} = \sum_j \left(\frac{1}{|\lambda_j|} + \frac{g}{\lambda_j} \right) \boldsymbol{C}_j\, {}^t\boldsymbol{C}_j. \tag{1}$$

The r-th diagonal component $s_{rr}^{(g)}$ of this matrix is the SD on site r, which is conventionally denoted by $S_r^{(g)}$. The BD between sites r and s is the off-diagonal component $s_{rs}^{(g)}$ of $\boldsymbol{S}^{(g)}$. Naturally, $\boldsymbol{S}^{(g)}$ is real-symmetric.

The bond order matrix $\boldsymbol{P}$ for the normal state mentioned above can be written in a well-turned form as[1)]

$$\boldsymbol{P} = \sum_j \frac{\lambda_j}{|\lambda_j|} \boldsymbol{C}_j\, {}^t\boldsymbol{C}_j. \tag{2}$$

The off-diagonal components of this matrix are bond orders, while the diagonal components are electron densities on sites measured from unity. Using $\boldsymbol{P}$ and the inverse of $\boldsymbol{A}$, we can decompose $\boldsymbol{S}^{(g)}$ as

$$\boldsymbol{S}^{(g)} = \boldsymbol{A}^{-1}\boldsymbol{P} + g\boldsymbol{A}^{-1}, \tag{3}$$

where the dependence of $\boldsymbol{S}^{(g)}$ on g is ascribed solely to $\boldsymbol{A}^{-1}$. When the system is alternant, $\boldsymbol{A}^{-1}$ and $\boldsymbol{P}$ have nonvanishing components only between different-color sites as well as $\boldsymbol{A}$, and $\boldsymbol{A}^{-1}\boldsymbol{P}$ does only between identical-color sites. Therefore, $s_{rs}^{(g)}$ is simply equal to either $(\boldsymbol{A}^{-1}\boldsymbol{P})_{rs}$ or $g(\boldsymbol{A}^{-1})_{rs}$, depending on whether the color of r and that of s are identical or not. BDs between

1) This bond order matrix differs form the p-density matrix (bond order electron density matrix) by the unit matrix.

identical-color sites as well as SDs are necessarily independent of g, denoted simply as s_{rs} as well as S_r.

Let σ_r stand for the color of r and let c_{rj} denote the site-r component of $\boldsymbol{C}_j$. Alternant symmetry enables us to rewrite the component of $\boldsymbol{A}^{-1}$ as

$$(\boldsymbol{A}^{-1})_{rs} = (1-\delta_{\sigma_r,\sigma_s})\sum_{j}^{\lambda_j>0} \frac{2}{\lambda_j} c_{rj} c_{sj}\,, \tag{4}$$

so that we can regard it as a kind of bond orders. This kind of bond orders is closely related to Kekulé structures (Ham and Ruedenberg, 1958; Ham, 1958; Isihara, 1996) called Rudenberg bond order. Since the component of $\boldsymbol{A}^{-1}\boldsymbol{P}$ can be naturally written as

$$(\boldsymbol{A}^{-1}\boldsymbol{P})_{rs} = \delta_{\sigma_r,\sigma_s}\sum_{j}^{\lambda_j>0} \frac{2}{\lambda_j} c_{rj} c_{sj}\,, \tag{5}$$

it is formally the same kind of bond orders as Rudenberg bond order, though it seems no longer to be related to Kekulé structures. BDs between identical-color sites can be nonvanishing, forming a striking contrast with bond orders between identical-color sites which necessarily vanish from alternant symmetry.

3. Analytic Expression

Consider the linear chain of m sites with m even. Number the sites consecutively from 1 to m and denote the set $\{1, \cdots, m\}$ of natural numbers by M. This system is alternant and we can assign one color to the odd-number subset M_{o} of M and the other to the even-number subset M_{e} of M. Let $\bar{r}$ stand for $m-r+1$. Then, site $\bar{r}$ is equivalent to site r from the symmetry of the system, but the color of $\bar{r}$ differs from that of r, namely, $\bar{r}$ belongs to M_{e} for $r \in M_{\mathrm{o}}$ and vice versa. Let us prepare the symbol $\tilde{r}$ indicating r for $r \in M_{\mathrm{e}}$ and $\bar{r}$ for $r \in M_{\mathrm{o}}$ for the sake of convenience.

The adjacency matrix $\boldsymbol{A}$ of this system is regular and the inverse $\boldsymbol{A}^{-1}$ can be easily calculated to provide BDs between different-color sites:

$$s_{rs}^{(g)} = \begin{cases} g(-1)^{(|r-s|-1)/2} & (r<s,\ r\in M_{\mathrm{o}} \ \text{ or } \ r>s,\ s\in M_{\mathrm{o}}) \\ 0 & (r<s,\ r\in M_{\mathrm{e}} \ \text{ or } \ r>s,\ s\in M_{\mathrm{e}}) \end{cases} \quad \begin{pmatrix} r,s\in M \\ \sigma_r \neq \sigma_s \end{pmatrix}. \tag{6}$$

Obviously, this quantity takes one of the three values 1, 0, and -1 without regard to m.

To deal with BDs between identical-color sites, it will be the best to utilize the reduction formula

$$s_{rs} = S_{(r+s)/2} - S_{|r-s|/2} \qquad (r \neq s \in M,\ \sigma_r = \sigma_s) \tag{7}$$

valid for linear chains. This formula follows from the hypervirial condition

$$[S^{(g)},\quad A] = 0 \tag{8}$$

upon BDs,[2)] exactly as the reduction formula for bond orders follows from the hypervirial condition upon bond orders (Isihara, 1991b). Since the derivation is completely similar, no description will be necessary about it here. Using the expression (Isihara, 1997)

$$S_r = \frac{1}{m+1}\sum_{k=1}^{\tilde{r}} \operatorname{cosec}\left(\frac{2k-1}{2m+2}\pi\right) \qquad (r \in M) \tag{9}$$

for SDs in the reduction formula above and arranging the summation index relevantly with the symmetry of cosecant, we obtain

$$s_{rs} = \frac{(-1)^{|r-s|/2}}{m+1}\sum_{k=|r-s|/2+1}^{(\tilde{r}+\tilde{s})/2} \operatorname{cosec}\left(\frac{2k-1}{2m+2}\pi\right) \qquad \begin{pmatrix} r,s \in M \\ \sigma_r = \sigma_s \end{pmatrix}. \tag{10}$$

This expression remains valid even if r and s coincide, namely, this includes the expression of SDs as a particular case. To evaluate one or some of BDs of a linear chain, this expression is certainly useful. However, if all of the BDs are required, we must use the reduction formula after evaluating all of SDs of the linear chain. The SDs can be evaluated quite efficiently by calculating S_r for $r \in M_e$ consecutively and by using the symmetry $S_r = S_{\bar{r}}$.

4. Basic Features

What we have to do here is only to read the expressions (Eqs. 6 and 10) of BDs obtained in the preceding section. The expressions are already so explicit and lucid that we will need no complicated argument. Furthermore, the reduction formula (Eq. 7) and the asymptotic estimates of SDs obtained in the previous paper (Isihara, 1997) are helpful to examine behaviors of BDs in long linear chains.

First, let us interpret behaviors of BDs between different-color sites on the unique Kekulé structure of a linear chain. Let ξ_{rs} and η_{rs}, respectively, denote the number of double bonds and that of single bonds between sites r and s in the Kekulé structure. Then, ξ_{rs} and η_{rs} necessarily differ by unity for different-color sites. If ξ_{rs} is larger, then $s_{rs}^{(g)}$ is either g or $-g$, depending on whether ξ_{rs} is odd (g) or even ($-g$). If η_{rs} is larger, $s_{rs}^{(g)}$ vanishes. A remarkable feature is that the absolute

2) The proof of this condition is trivial. For linear chains, this condition yields another formula reducing BDs between distant sites of different colors to differences between adjacent-site BDs. We may use it to obtain the inverse of the adjacency matrix.

value of nonvanishing $s_{rs}^{(g)}$ remains unity for different-color sites without regard to m.

Next, let us proceed to BDs between identical-color sites. Let d_{rs} denote the distance $|r-s|$ between sites r and s. Since s_{rs} is a cumulative sum of positive cosecant terms multiplied by the whole sign factor $(-1)^{d_{rs}/2}$, s_{rs} is positive if d_{rs} is a multiple of 4, and negative if d_{rs} is an even number, not a multiple of 4.

Note that, aside from the sign factor, s_{rs} depends on r and s only through the initial and the final values of the summation index, and that they contain $r+s$ and d_{rs} separately. With the distance d_{rs} fixed at d, we find that the "end" BD

$$s_{1,1+d} = \frac{(-1)^{d/2}}{m+1} \sum_{k=d/2+1}^{m-d/2} \operatorname{cosec}\left(\frac{2k-1}{2m+2}\pi\right) \qquad (m-2 \geq d \in M_{\mathrm{e}}) \tag{11}$$

is the maximum for even $d/2$ and the minimum for odd $d/2$, while the "next-end" BD

$$s_{2,2+d} = \frac{(-1)^{d/2}}{m+1}\left(\operatorname{cosec}\left(\frac{d+1}{2m+2}\pi\right) + \operatorname{cosec}\left(\frac{d+3}{2m+2}\pi\right)\right) \qquad (m-2 \geq d \in M_{\mathrm{e}}) \tag{12}$$

is the minimum for even $d/2$ and the maximum for odd $d/2$. Now, let the center $(r+s)/2$ be fixed at c and let $|r-s|/2$ be a variable w. Naturally, we can assume $m \geq 4$ and $w \geq 1$. It is obvious that $s_{c-w,\,c+w}$ attains the minimum at odd w as small as possible and the maximum at even w also as small as possible. Hence, $s_{c-1,\,c+1}$ is always the minimum. If $m \geq 6$, then $s_{c-2,\,c+2}$ is the maximum under the assumption that $c-2 \geq 1$ and $c+2 \leq m$. Thus, provided that $m \geq 6$, the largest and the smallest of BDs between identical-color sites are $s_{1,5}$ and $s_{1,3}$, respectively. The absolute values of these BDs become large as m increases: $s_{1,5}$ exceeds unity with $m=18$ and $|\,s_{1,3}\,|$ does with $m=12$.

Lastly, let us examine asymptotic behaviors of BDs in long linear chains. As m becomes large with d left fixed, the next-end BD converges as

$$\lim_{m\to\infty} s_{2,2+d} = (-1)^{d/2}\frac{2}{\pi}\left(\frac{1}{d+1} + \frac{1}{d+3}\right) \qquad (m >> d \in M_{\mathrm{e}}). \tag{13}$$

For example, the maximum $s_{2,4}$ for d=2 converges to $-16/15\pi$ (≈ -0.34) and the minimum $s_{2,6}$ for d=4 converges to $24/35\pi$ (≈ 0.22). On the other hand, the end BD diverges, since the final value of the summation index includes m. To see this situation, it may be appropriate to return to the reduction formula. We have only to note that SDs on odd sites near site 1 as well as S_1 are logarithmically divergent and that SDs on even sites near site 1 are convergent. In the reduction formula

$$s_{2,2+d} = S_{d/2+2} - S_{d/2} \tag{14}$$

both of the two SDs are either divergent or convergent, while in

$$s_{1,\,1+d} = S_{d/2+1} - S_{d/2} \tag{15}$$

one of the two SDs is logarithmically divergent and the other convergent.

Asymptotic estimates for the end BD are derivable from relevant asymptotic estimates of SDs in long linear chains (Isihara, 1997). Say, up to the first order of m^{-1}, we have

$$s_{1,\,1+d} \cong (-1)^{d/2}\frac{2}{\pi}\left(\ln m + D - \phi(d) + m^{-1}\right) \qquad (m >> d \in M_{\mathrm{e}}) \tag{16}$$

with

$$D = \ln(8/\pi) + \gamma \text{ (Euler's constant)} \approx 1.51193 \tag{17}$$

and

$$\phi(d) = 2\sum_{k=1}^{d/2}\frac{1}{2k-1} + \frac{1}{d+1}. \tag{18}$$

Now, suppose that identical-color sites r and s are, respectively, near site 1 and site m. Then, $|r-s|/2$ as well as $(r+s)/2$ must be approximately $m/2$. Therefore, the asymptotic estimate of SDs in the middle of long linear chains (Isihara, 1997) leads us to

$$S_{(r+s)/2} \cong S_{|r-s|/2} = \frac{1}{\pi}(\ln m + D) + \mathrm{O}(m^{-1}) \tag{19}$$

and, through the reduction formula, we have

$$\lim_{m\to\infty} s_{rs} = 0 \qquad\qquad (r << m,\ \ m - s << m,\ \ \sigma_r = \sigma_s). \tag{20}$$

That is to say, as linear chains become long, BDs between a site near one end and an identical-color site near the other end tend to zero.

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